Relating Ocean Optics to Photochemical Transformations of Dissolved Organic Carbon in Coastal Waters

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LONG-TERM GOALS

The long-term goal of this research is to use remotely sensed ocean optical data for estimates of the regional and global scale significance of photochemistry to dissolved organic carbon (DOC) cycles and optical changes resulting from these processes.

OBJECTIVES

The central objective of this research program is to examine quantitatively the links between optical measurements and photochemical carbon transformations in the sea. Our goal is to establish quantitative methods to relate variability in water-leaving radiance to photochemical reactions that lead to direct loss of colored dissolved organic matter (CDOM) and consequent changes in UV optical properties in the photic zone. By examining these quantitative relationships, we also hope to gain both an understanding of the dominant variables controlling UV optics in the mixed layer and the critical parameters influencing DOC photochemical reactions in seawater.

APPROACH

To achieve the objectives stated above requires a wavelength dependent description of the *in situ* optical field for ultraviolet radiation (UV) together with spectral efficiency data for photooxidation of CDOM. Our general approach uses three connected principles:

(1) Diffuse attenuation coefficients for visible spectral irradiance can be related to ocean color (i.e., ratios of near-surface water-leaving radiance; Austin and Petzold 1981). Our results from previous work indicate that comparable relationships between water-leaving radiance in the visible and diffuse attenuation of UV radiation can also be determined.
(2) CDOM is the dominant contributor to the absorption and attenuation of UV in coastal waters. With appropriate caution, and proper accounting for adsorption by particles, diffuse attenuation of UV can be related directly to absorption by dissolved organic matter.
(3) The absorption of UV by CDOM leads to photochemical transformations that include the destruction of chromophores and production of lower-molecular weight compounds. Wavelength-dependent quantum yields (QY) for these transformations can be determined experimentally.

Given measurements of solar radiation and upwelling radiance at the sea-surface, we will estimate photochemical transformations of surface-layer DOM by applying empirical relationships between: (1)

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reflectance and diffuse attenuation, (2) spectral diffuse attenuation and UV absorbance, and (3) UV absorbance and action spectra for photochemical transformations.

Field optical data are collected with two instruments (Satlantic, Inc.) that add UV measurements to visible wavebands compatible with the SeaWiFS ocean color satellite. The first is a modified Tethered Spectral Radiometer Buoy (TSRB-II) which simultaneously measures incident irradiance (Ed) and upwelling radiance (Lu) in 14 wavebands, including 4 in the UV (2 nm bandwidth). The second is a SeaWiFS Profiling Multichannel Radiometer (SPMR) which measures vertical profiles of downwelling irradiance in wavebands identical to the TSRB-II, chlorophyll fluorescence (WETStar miniature flow through fluorometer), conductivity, and temperature. Both instruments are deployed simultaneously to accumulate UV/VIS optical data (Ed, Lu, & Kd) while collecting discrete rosette samples at the same station for evaluation of CDOM absorption.

Laboratory irradiations (both on shore and at sea) are used to quantify the efficiency of photochemical carbon mineralization. Using a broad-spectrum xenon lamp, a series of sequential long-pass optical filters, and a statistical evaluation (Rundel, 1983) of the resulting photochemical rates, we calculate a QY spectrum for photochemical and coincident physical/chemical (ex. fading) alterations of the CDOM with a single irradiation. This represents a novel approach to photochemical QY determinations that is much faster than other monochromatic approaches (3 hrs vs. 3 weeks). This allows evaluation of both spatial and temporal variations in QY spectra, not previously possible with other approaches. By combining spectral photochemical efficiency data, absorbance data, irradiation profiles, and solar spectral irradiance, we can calculate both whole water column and depth discriminated photochemistry.

Using relationships developed by deployments of the TSRB-II and SPMR with discrete measurements of CDOM absorptivity, we will combine remotely sensed data with irradiance and water optical models to estimate the photomineralization of CDOM in the coastal ocean. These data will represent the beginning of regional photochemical inventories and a starting point for long term regional scale studies of photochemical carbon transformations in the coastal ocean.

At Dalhousie, Bill Miller (PI), Penny Kuhn (technician), two graduate students, Sophie Johannessen (Ph.D.) and Lori Ziolkowski (M.Sc.), have the ONR project as their primary effort. Our field optical component benefits greatly from the participation of J.J. Cullen's group (w/ R. Davis) also at Dalhousie and assistance from Satlantic, Inc. (instrument development, optical expertise, field and computer assistance). This year, our field collaborations were with (1) a Norwegian group (H. Browman, B. Kjeldstad, S.R. Erga, and T. Svenøe) in a UV intercalibration exercise, (2) D. Kieber and K. Mopper (NSF funding) by sharing shiptime and field data, and (3) M. A. Moran and R. Zepp (ONR funding) in a photochemical/microbial interaction study at Sapelo Island Marine Lab, GA.

WORK COMPLETED

We staged for and participated in two cruises and one field study at a land based research facility. These efforts included successful completion of both laboratory irradiations (on land and at sea) and collection of *in situ* optical data.

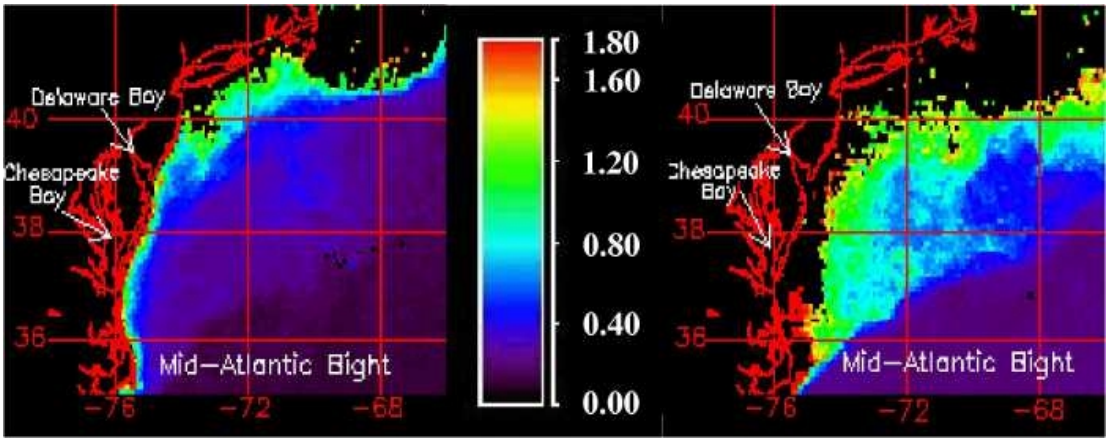
We developed and constructed a new sequential long band-pass filter irradiation box to hold 10 cm spectrophotometer cells at constant temperature, a great improvement for CDOM fading applications.

We generated QY spectra for CO_2 (n=14) & CO (n=20) photochemical production in the coastal ocean and a preliminary photochemical efficiency surface for CDOM fading.

We developed/modified MATLAB® code that efficiently generates QY spectra from experimental data and assembled a preliminary mixed layer model that predicts CDOM fading in coastal waters.

RESULTS

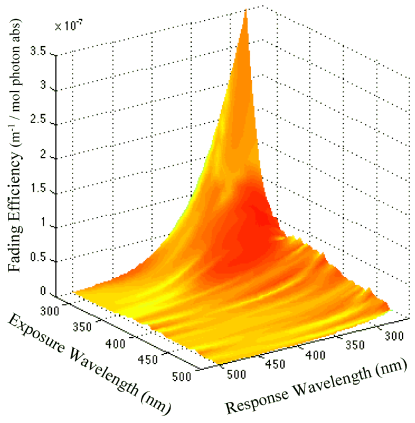
We have continued to accumulate samples and optical data from diverse water types in an effort to build robust optical relationships that will be useful in predicting photochemistry from remotely sensed data. This year, we added to our optical data set with deployments in the Gulf of Maine and Samnanger Fjord, Norway. Using the data set amassed over the last three years, we have generated algorithms (relating Kd at 323, 338, and 380 nm to $Lu_{412/555}$) that allow estimates of *in situ* UV attenuation to be made from remotely sensed ocean color in the visible. As part of her thesis, Sophia Johannessen has produced regional maps (Figure 1 for example) from SeaWiFS data. These match our Kd field data from the same location (n=4, image and samples from July 1998) to within 10% for Kd_{323}. These results will be submitted for publication before the end of 1999. We are proceeding to calculate photochemical rates for CO_2 and CO production over regional scales using quantum efficiencies determined as part of this project (see below).



1. Estimates for Kd at 323 nm in the Mid-Atlantic Bight made from SeaWiFS data.

The irradiation box constructed last year (15 long-pass filters over custom quartz containers) was used for quantum yield determinations for CO_2 and CO photochemical production. CO_2 efficiency increases dramatically offshore while CO efficiency appears to remain constant, suggesting different production mechanisms relative to CDOM fading dynamics. Both of these results were accompanied by further development of MATLAB® code to achieve more flexible application of the fitting functions to our quantum efficiency calculations. We also extrapolated the Rundel approach to construct a preliminary 1 nm resolution, 3-dimensional quantum efficiency surface for CDOM fading (250 separate QY curves) using a sample from the Northwest Arm, Halifax, Nova Scotia. This result is shown in Figure 2. From this surface, a quantitative model of CDOM fading kinetics was developed which incorporates three

linked modules (radiative transfer, surface layer mixing, and photochemical processes). The model provides a reasonable estimation for CDOM spectral changes (280nm – 500nm) in a coastal setting.



2. Photochemical efficiency surface for CDOM fading

IMPACT / APPLICATIONS

The optical properties of CDOM in the ocean control photochemical rates, effect oceanic chemical cycles, and influence the interpretation of ocean color (Miller, 1998). Based on data from the field, we feel that instrumentation capable of characterizing UV radiation in the surface ocean will prove invaluable to the understanding of the variability in the CDOM signal. Our preliminary approach to modeling CDOM fading is similar enough to field observations to argue that additional effort will produce a critical component toward predictive capability for CDOM dynamics. While a large effort is still needed on both optical and photochemical research fronts, the approach developed thus far appears to be sound and should lead to novel and critical insight on the link between ocean optics and photochemical carbon transformations. It will also result in the unique ability to address the regional and global significance of photochemical reactions in the ocean.

TRANSITIONS

Based on the utility of the optical system we have assembled, we have received offers to participate with several groups interested in other photochemical processes. This will continue to produce opportunities to add varied water types to our expanding optical database and provide samples for photochemical evaluation. Development of new MATLAB® algorithms (in collaboration with J.J. Cullen and R. Davis) will provide novel tools to expand quantitative evaluations of photochemistry to new groups in marine chemistry. These numerical approaches relieve many of the time constraints previously present in photochemical studies and will make spatial and temporal evaluation of CDOM dynamics feasible.

RELATED PROJECTS

As stated above, we have collaborated with three groups on fieldwork to obtain optical data, *in situ* photochemical data, and data on the interaction between photochemical transformations and microbial impact on CDOM. Work by M. Lewis (ONR), also at Dalhousie, in his study of bio-optical variability

and development of novel optical instrumentation along with J.J. Cullen efforts on optical models, data analysis, and instrument development are closely related to this project. The timely development of both our novel Satlantic instruments and numerical modeling approaches depends heavily on these relationships.

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